

DESTRUCTION AND DISPOSAL OF
CANADIAN STOCKS OF WORLD
WAR II MUSTARD GAS

R.S. WEAVER, C. REICHERT and S.B. MELLESEN

**Defence Research
Establishment
Suffield.**

SPECIAL PUBLICATION N° 67

DEFENCE RESEARCH ESTABLISHMENT SUFFIELD
RALSTON ALBERTA

SUFFIELD SPECIAL PUBLICATION NO. 67

DESTRUCTION AND DISPOSAL OF CANADIAN STOCKS OF
WORLD WAR II MUSTARD GAS

by

R.S. Weaver, C. Reichert and S.B. Mellisen

PROJECT NO. 99-30-15

December 1975

WARNING

The use of this information is permitted subject to recognition
of proprietary and patent rights".

DEFENCE RESEARCH ESTABLISHMENT SUFFIELD
RALSTON ALBERTA

SUFFIELD SPECIAL PUBLICATION NO. 67

DESTRUCTION AND DISPOSAL OF CANADIAN STOCKS OF
WORLD WAR II MUSTARD GAS

by

R.S. Weaver, C. Reichert and S.B. Mellisen

ABSTRACT

Early in World War II, over 700 tons of the chemical warfare agent mustard were shipped from Cornwall, Ontario, to the Defence Research Establishment Suffield, and stored in lead-lined concrete vaults. Research was begun several years ago to find a safe, efficient, environmentally acceptable and economical method of disposing of this still hazardous material. Laboratory studies led to the discovery that, with turbulent mixing and proper control of temperature and acidity, mustard would react with water to produce a non-vesicant hydrolysate mixture. These results were extended and the process further optimized in pilot plant runs, involving a total of several tons of mustard. It was also demonstrated that the hydrolysate could be burned completely in a specially modified incinerator.

DEFENCE RESEARCH ESTABLISHMENT SUFFIELD
RALSTON ALBERTA

SUFFIELD SPECIAL PUBLICATION NO. 67

DESTRUCTION AND DISPOSAL OF CANADIAN STOCKS OF
WORLD WAR II MUSTARD GAS

by

R.S. Weaver, C. Reichert and S.B. Mellisen

BACKGROUND

Since 1942, over 700 tons of the chemical warfare agent mustard have been held in storage in liquid bulk form at the Defence Research Establishment Suffield (DRES). This mustard was manufactured at Cornwall, Ontario, and shipped to Suffield, Alberta during the Second World War for storage for contingency purposes. Fortunately this agent was not required during the war.

For many years, the Canadian Government and the Department of National Defence (DND) have had no foreseeable need for, nor interest in retaining, this now obsolete stockpile of chemical agent and DRES was requested to investigate methods for its destruction.

INTRODUCTION

Mustard is a very hazardous material to work with, and extreme caution is essential. Minute droplets can permanently damage eyesight and will penetrate conventional clothing, causing serious blisters and skin burns which are very slow to heal. Mustard vapour can have effects on the skin, eyes and lungs. It was fitting that DRES be given the task of disposing of these mustard stocks. Not only was the material stored at this Establishment, but DRES has facilities and experience unique in Canada for dealing with highly toxic and hazardous materials. DRES also has scientific expertise and personnel, such as chemists, toxicologists and engineers, required to support such an undertaking.

In all of the subsequent applied research and engineering studies concerned with disposal of mustard, the main criteria for the entire process were:

1. The process must be totally safe.
2. The process must be effective in destroying the mustard.
3. The process must comply with Government environmental standards.
4. The cost of equipment, materials and labour must be within the somewhat limited resources which could be diverted to this task.

GENERAL INVESTIGATIVE APPROACHES

Shortly after World War II, several countries disposed of mustard stocks by dumping them in the ocean and by open pit burning. Neither of these methods is acceptable by environmental standards of today. When the DRES study began, the only country known that had recently destroyed mustard was the United Kingdom, and they were very helpful in providing information on their disposal process. They had a relatively small facility which destroyed the mustard by burning, followed by scrubbing of the corrosive gases produced. This proved satisfactory for their needs, but their facility was totally inadequate for the much larger quantities held in storage at DRES.

Our Establishment was fortunate in having a large incinerator, or "Thermal Destructor", which had been developed earlier with the help of Canadian industry. This had been used for the disposal of the total Canadian stocks of liquid DDT mixtures, amounting to some 750 tons (about the same as the mustard stocks). As a result of some applied research work at DRES, and based on the United Kingdom experience, it was concluded that there would be no basic scientific or engineering problems to overcome in the direct burning of mustard using the existing Thermal Destructor. Extensive engineering changes, however, would have been required to ensure that the extra operation could be carried out in an entirely safe manner. As part of this safety requirement, it would have been necessary to move the complete Thermal Destructor facility to a more remote location with all the attendant problems of construction engineering and utilities services. There was also concern with the problems of facility maintenance after the Destructor had been used for disposing of mustard.

It was decided to search for a new chemical process which would allow conversion of the mustard into a non-hazardous material. A prime requirement of any such process was that it lend itself to engineering expansion into a large facility which would be totally safe and effective. After considerable laboratory work, a batch process was developed which appeared to be relatively low cost and which lent itself well to scaling up in size; it also appeared to resolve the problem of disposing in a safe manner, and in a reasonable time, of the entire stocks of mustard. The principles are relatively simple: the process involves the vigorous stirring, at high temperatures, of the mustard with two additives, water and slaked lime (calcium hydroxide). These two materials are needed in large quantities but are fortunately among the lowest priced materials possible. The resultant hydrolysis product is a liquid which is relatively non-toxic, safe and easy to handle. The entire process will be described in more detail later.

Limited experiments were also carried out on chemical methods of converting the mustard directly into an insoluble and non-hazardous solid. These were successful from a scientific standpoint, when a method was evolved to react the mustard with sodium sulphide. However, it became apparent that the engineering problems of ensuring that no unreacted mustard was trapped in the solid as it was formed would be considerable. Further, the costs of the required large quantities of sodium sulphide were quite high. Consequently, further consideration of this method was dropped.

The initial laboratory work on mustard hydrolysis was done with very small (i.e. less than one gram) quantities of mustard. These quantities were gradually increased as the optimum ratios of mustard, water and lime, operating conditions, etc., were determined. Next, pilot-scale experiments were carried out in the field, where it was safe to work with larger quantities of mustard (up to 1000 pounds) at a batch. This concept was finally engineered into a facility located on top of the mustard storage vaults and controlled from a nearby instrumented shack. The first full-scale trials were carried out in June 1974 and routine operations are now underway. The facility which now exists totally destroys one batch of about 16,000 pounds (or 8 tons) of mustard in a day with one shift operation; however, normally a double batch of about 16 tons is done in a 12-hour day. After each run, laboratory analyses are used to confirm that no significant amount of mustard remains, and the waste product, called "hydrolysate", is dumped from the reaction vessel into one of the empty mustard vaults for subsequent disposal. (During World War II, ten reinforced concrete, lead-lined vaults were constructed for storage purposes, but only four were ever used for the actual storage of mustard. These vaults have inside dimensions of 35 feet by 20 feet and are 12 feet in height. They are about one-half below ground level and each has two circular access ports on the top).

The hydrolysate was determined by DRES toxicologists to be non-hazardous, and could now be disposed of without all of the attendant safety engineering problems which would have been associated with the destruction of the mustard itself. The hydrolysate produced from pilot-scale batches was used in the fall of 1974 in a number of trials to test whether the liquid waste product could be burned successfully in the Thermal Destructor. This approach was found to be feasible as a final step in the mustard disposal problem. However, even this operation required some modifications to the Destructor and requires considerable labour for manning the facility on a 24-hour day basis. Consequently, it was deemed prudent to investigate whether some simpler, but yet environmentally acceptable, disposal method for this non-hazardous liquid was possible.

Serious consideration was given to merely hauling the liquid waste product and dumping it into a pit on the DRES experimental range and covering it over with earth. As part of an earlier study concerned with the long-term recoverable storage of radioactive wastes, extensive hydrological and surficial geological studies were completed of a near optimum location on our range for disposal of this type of waste. The results of this study established that the particular site is perhaps one of the best "landfill sites" in Canada, both because of the soil itself and because the average rainfall in this area is extremely low (for the last thirty years, the average yearly total precipitation has been only 11.6 inches). Experiments were carried out on a small scale to demonstrate that essentially total containment of the liquid would be provided by the soil at this particular site.

It was recognized from our discussions with environmental experts that this landfill method would be more readily acceptable if a solid material which was relatively insoluble in water was being disposed of. Consequently some experiments were carried out using ordinary Portland Cement, to convert the hydrolysate into a concrete-like material for disposal. The

results were encouraging but would have involved the installation of a relatively large concrete mixing facility to cope with the large quantities of hydrolysate.

DRES microbiologists also participated in this program by studying the rates of biodegradation of the hydrolysate waste product if it was thinly spread over a small portion of our range. Again the biodegradation rates were encouraging and the hydrolysate did not seem to have significant effects on the vegetation.

With all this information on various methods for disposing of the hydrolysate, it appeared an appropriate time to obtain opinions from outside experts on the environmental acceptability of the various schemes. Here the concerns were not only with the view of government authorities, but also that the public at large would agree that whatever disposal operations were undertaken were as "clean" as it was sensible to be.

It was decided to hold an environmental seminar and workshop to discuss the various approaches to disposal of the waste product. In addition to the DRES scientific staff, a number of representatives were present from Environment Canada and from the Department of the Environment for the Province of Alberta, several University Professors, Alberta Research Council experts and a consultant from industry. This was a very stimulating and worthwhile meeting. Most of the experts felt that the landfill and biodegradation approaches were acceptable; however, the more conservative participants felt quite strongly that more research was needed into the environmental acceptability of the proposals. These further research studies that would have been needed were extensive, and would have cost more in time and effort than proceeding with the more straightforward route of thermal destruction of the waste product. It was gratifying that this approach received the unanimous support of the environmental experts who stipulated only that our Thermal Destructor be modified and operated to comply with government "clean-air" regulations.

Thus, as a result of all the applied research work which was carried out at DRES and the advice received from independent environmental experts, a two-phase disposal scheme was adopted and is now in operation. This consists of:

Phase 1: Converting the mustard by a batch chemical process into a non-hazardous material (this step requires 4 operating personnel per batch),

followed by

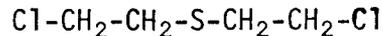
Phase 2: Incineration of the resultant waste product by use of the modified DRES Thermal Destructor (this requires 2 operating personnel per 8-hour shift on a continuous basis).

MUSTARD HYDROLYSIS AND DISPOSAL OPERATIONS

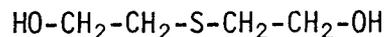
The preceding discussion outlined in general how we arrived at a mustard disposal process which met our somewhat demanding initial goals,

namely that the process must be safe, completely effective, meet Government environmental standards, and be relatively inexpensive. The steps in the disposal process will now be described in greater detail.

First, a brief description of the chemistry of the mustard hydrolysis step is appropriate. Mustard is a fairly simple molecule, containing carbon, hydrogen, sulfur and chlorine atoms (see Figure I), represented schematically as:



During hydrolysis, the chlorine atoms are replaced by "hydroxyl (OH)" groups, obtained from molecules of water, forming



This substance is called thiodiglycol; it is a member of the same chemical family as the ethylene glycol used in automobiles as antifreeze. Thiodiglycol is used in the textile industry; its toxicity is very low - quite similar to that of ethyl alcohol. The hydrolysate produced contained mostly thiodiglycol, some polysulfides from the impurities in the mustard, and calcium chloride (CaCl_2) formed by the neutralization of the HCl produced in the reaction. This hydrolysate was thoroughly tested at DRES on animals and on humans, and found to be completely non-vesicant (i.e., does not form blisters). However, it does have a very unpleasant odour.

The development and control of this hydrolysis reaction was an important breakthrough, and provided the key to the entire disposal process. A brief history of its evolution might prove interesting.

It has been known for some time that mustard dissolved in water reacts at a rate such that half of the dissolved mustard is hydrolyzed in 8 minutes at 25°C. It was also known that mustard would remain in contact with water for years with no appreciable change or disappearance. The DRES scientists decided to investigate this apparent inconsistency. If mustard and water are mixed, practically all of the mustard falls to the bottom of the mixture (mustard is only slightly soluble in water, and is 30% denser). It was found that at an interface between mustard and water, a minute amount of mustard reacts with the water, producing a thin "skin" of thiodiglycol plus hydrochloric acid (HCl). This skin prevents further solution of the mustard in the water, and no more mustard is hydrolyzed. It was then found that if the mixture was stirred vigorously at all times, and simultaneously a base such as calcium hydroxide (slaked lime) was added to neutralize the HCl produced, the mustard-water reaction would proceed rapidly. The final reaction process then was based on three principles: addition of calcium hydroxide to neutralize the HCl as fast as it is produced; vigorous stirring of the mixture to disperse the calcium hydroxide and mustard throughout the mixture; and operating the reaction at temperatures near 95°C, since the chemical reaction proceeds faster at higher temperatures.

Figures II, III and IV are attached to show the basic mustard reaction vessel and auxiliary equipment, and to illustrate how the above techniques are put into practice. Figure V shows a plot of temperature and pH (a measure of acidity) versus time during a typical batch run of mustard

hydrolysis. Note that both parameters are kept within certain limits; this is the method by which the reaction is controlled. This figure is reproduced from an early run in which 1000 gallons (about 6.5 tons) of mustard were hydrolyzed. Reaction time per batch, pH and temperature control, etc., have all been improved, and present runs normally involve 8 tons per batch, with two batches in a 12-hour day.

The prime consideration in the hydrolysis operation is that of safety. Mustard is such a hazardous substance to handle that as much thought and effort went into the safety aspects of the hydrolysis process as into the actual mechanical design. For example, every temperature sensor, stirring motor, liquid level indicator, etc., is duplicated. Spare components are on hand for all equipment. There is a fence around the mustard vault-reaction vessel area, and all hydrolysis operations are carried out remotely from outside the fence. If for any reason someone must go inside the fenced area, he must be dressed in protective clothing. Two basic assemblies of clothing are used, depending on the degree of protection required. The first consists of two protective layers, pyjamas under a Canadian chemical protective overgarment, plus rubber boots and gloves and a respirator. The second assembly is similar, with the addition of full rubber over these first two layers. The latter dress is very good for protection from mustard, but working time at high temperatures is limited (e.g. only 15 minutes at 30°C), because the body heat generated inside cannot be dissipated. The person entering the so-called "dirty" area, in this clothing, enters through the only open gate, is checked in and watched by a safety backup man and is carefully decontaminated and undressed before he leaves the "dirty" area again. Many other safety systems and equipments are available, e.g., for fires, chemical spills, vapour detection, electric power failure, etc.

Now, when a batch of hydrolysate is produced, tested for no mustard content, and dumped in the temporary storage vault, it is ready for transport to the Destructor for incineration. This is done by pumping it from the other end of the storage vault into a tanker, and hauling it to the Destructor which is located about 1 1/2 miles away. (Personnel involved in handling hydrolysate normally wear a chemical protective overgarment and respirator, not because the hydrolysate is hazardous, but because of its overpowering odour, and because even after washing, the odour remains on clothing that has had hydrolysate spilled on it.) At the Destructor, the tanker contents are unloaded into a holding tank and the material is then pumped and burned essentially as DDT used to be.

Since 1971, a "Thermal Destructor" has been in operation at DRES, as a consequence of a 1970 Canadian Government decision to ban general use of DDT; the Department of National Defence and Environment Canada had sent to DRES for destruction all of the Canadian stocks of DDT liquid formulations. A number of trials showed that mustard hydrolysate could be incinerated in the Destructor at reasonable burn rates, provided an additional smokestack was added to enable compliance with Clean Air Act standards. This stack was constructed at DRES and emplaced in September/October 1974. Figure VI shows the exterior of the Destructor complex with this 100-foot stack.

In operation, the Destructor (shown schematically in Figure VII) has the hydrolysate atomized and injected into a natural gas flame. The hydrolysate is burned completely, and the only combustion products of concern

are hydrochloric acid (HCl) gas and sulfur dioxide (SO₂). The effluent gases from the incineration pass through a water scrubbing tower, which removes all of the HCl and over 80% of the SO₂. (The effluent water is neutralized and recirculated.) The remaining SO₂ is dispersed into the atmosphere by the 100-foot smokestack. We have been assisted in Destructor trials and operations by Western Research and Development Limited of Calgary; this company was also hired to operate the Destructor initially, and to monitor SO₂ emission rates during hydrolysate burning. Hydrolysate is burned at a rate of up to 3 gallons per minute; the actual burn rate is adjusted depending on meteorological conditions such that ground level concentrations of SO₂ do not exceed the limits set out in the Canada Clean Air Act.

CONCLUSIONS AND SUMMARY

A relatively inexpensive process has been developed, capable of hydrolyzing 15 tons per day or more of mustard. The resultant hydrolysate waste product is non-hazardous, and can be disposed of in several ways. Partly because of existing facilities, it was decided to burn this material; this is being done at present, in compliance with environmental air standards.

By 23 October 1975 some 380 tons of mustard had been hydrolyzed, with 115,000 gallons (equivalent to 210 tons of mustard) of hydrolysate burned in the Destructor. Mustard hydrolysis is difficult to carry out during very cold weather, but it is anticipated that hydrolysis and burning of all the mustard stocks should be completed by summer 1976.

FIGURE I: REACTIONS OCCURRING IN MUSTARD HYDROLYSIS VESSEL

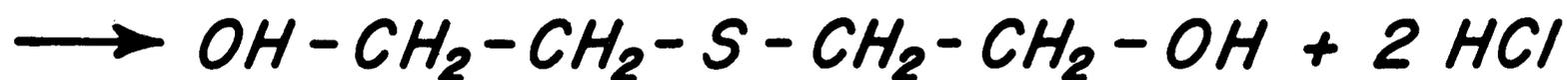


FIGURE II:

1. MUSTARD STORAGE VAULTS
2. CONTROL BUILDING
3. DECONTAMINATION COMPLEX
4. LIME AUGER
5. HYDROLYSIS REACTION VESSEL
6. HYDROLYSATE TRANSPORTER

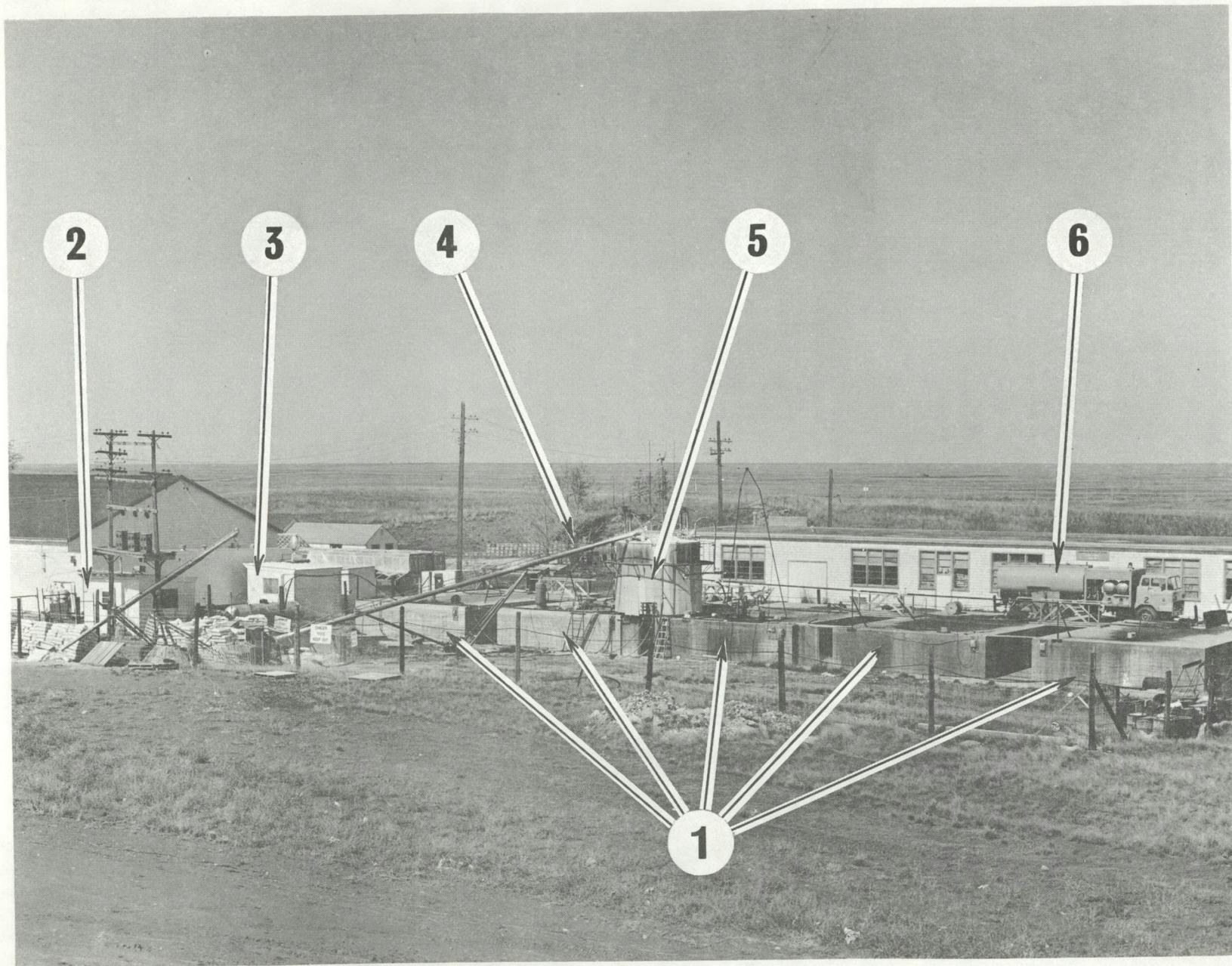


FIGURE III:

1. LIME AUGER
2. LIGHTNING ROD
3. AEROVANE
4. MUSTARD PUMP
5. HEATED MUSTARD DELIVERY LINE
6. WATER INLET LINE
7. STEAM INLET MANIFOLD

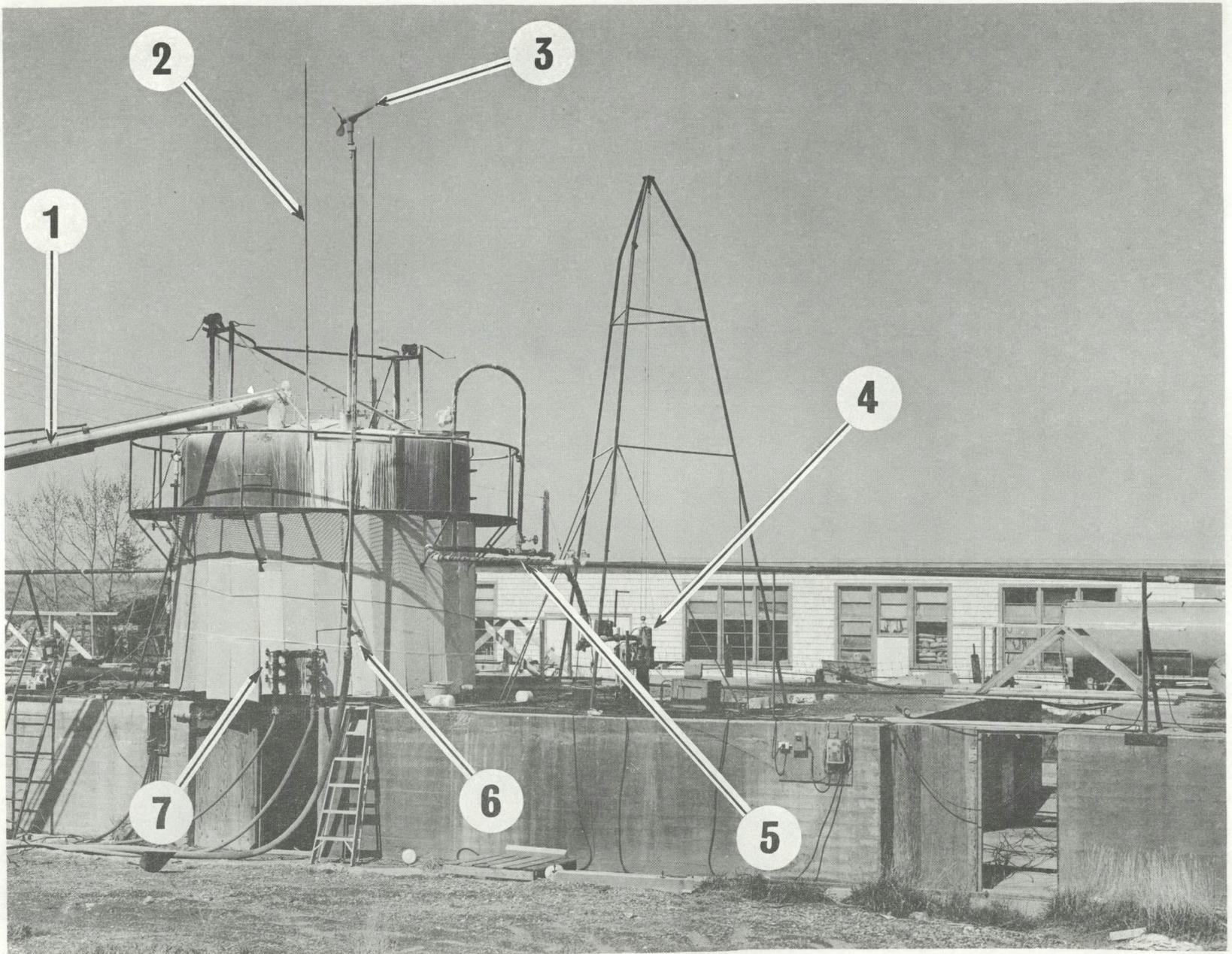


FIGURE IV:

1. pH PROBE
2. LEVEL INDICATOR
3. STIRRING MOTOR
4. WATER INLET LINE
5. LIME AUGER
6. STEAM INLET MANIFOLD
7. RECIRCULATING AND SAMPLING LINE
8. HYDROLYSATE DUMP VALVE
9. STIRRING MOTOR
10. STYROFOAM INSULATION

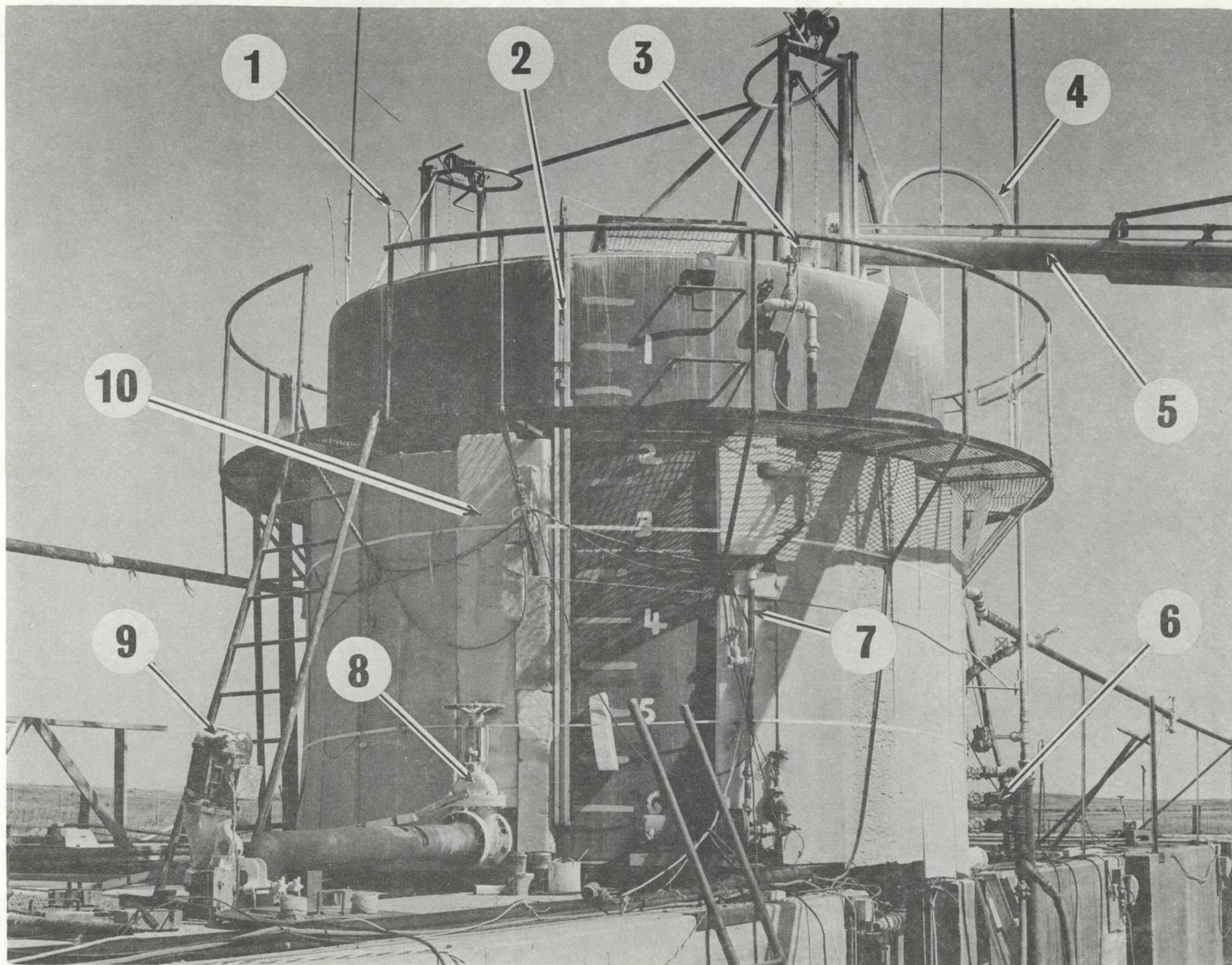


FIGURE V: TEMPERATURE AND pH RECORD OF A TYPICAL
MUSTARD HYDROLYSIS RUN

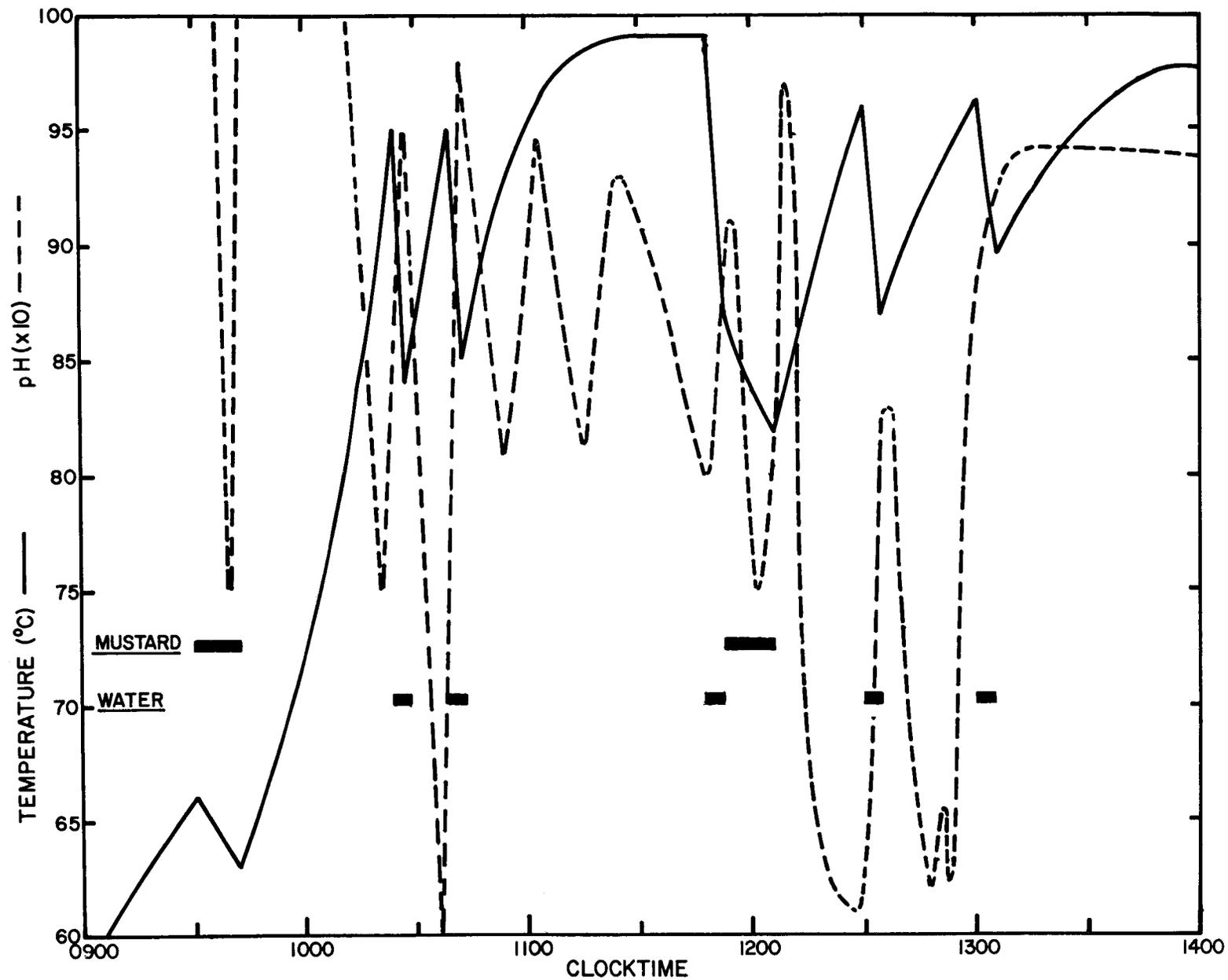
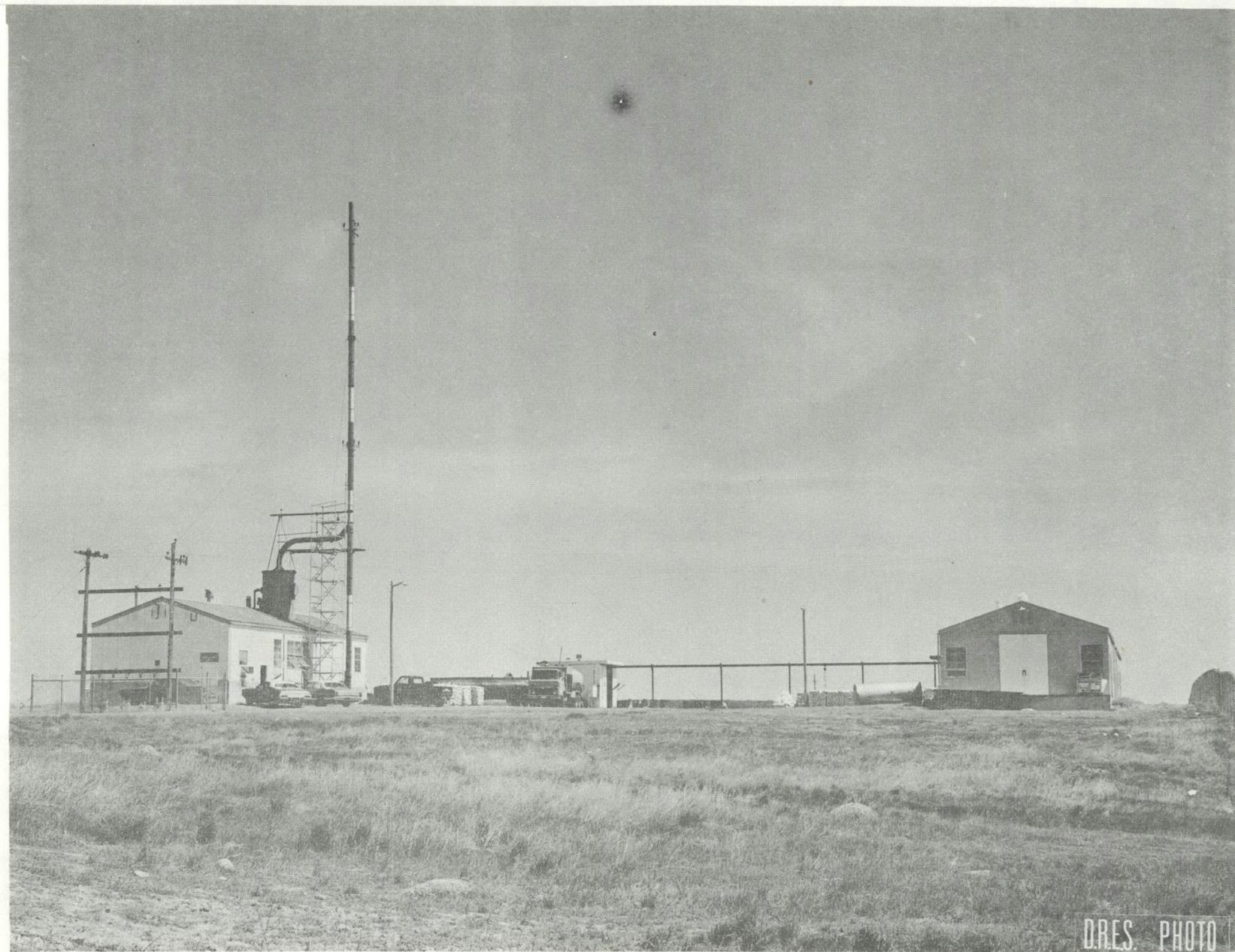
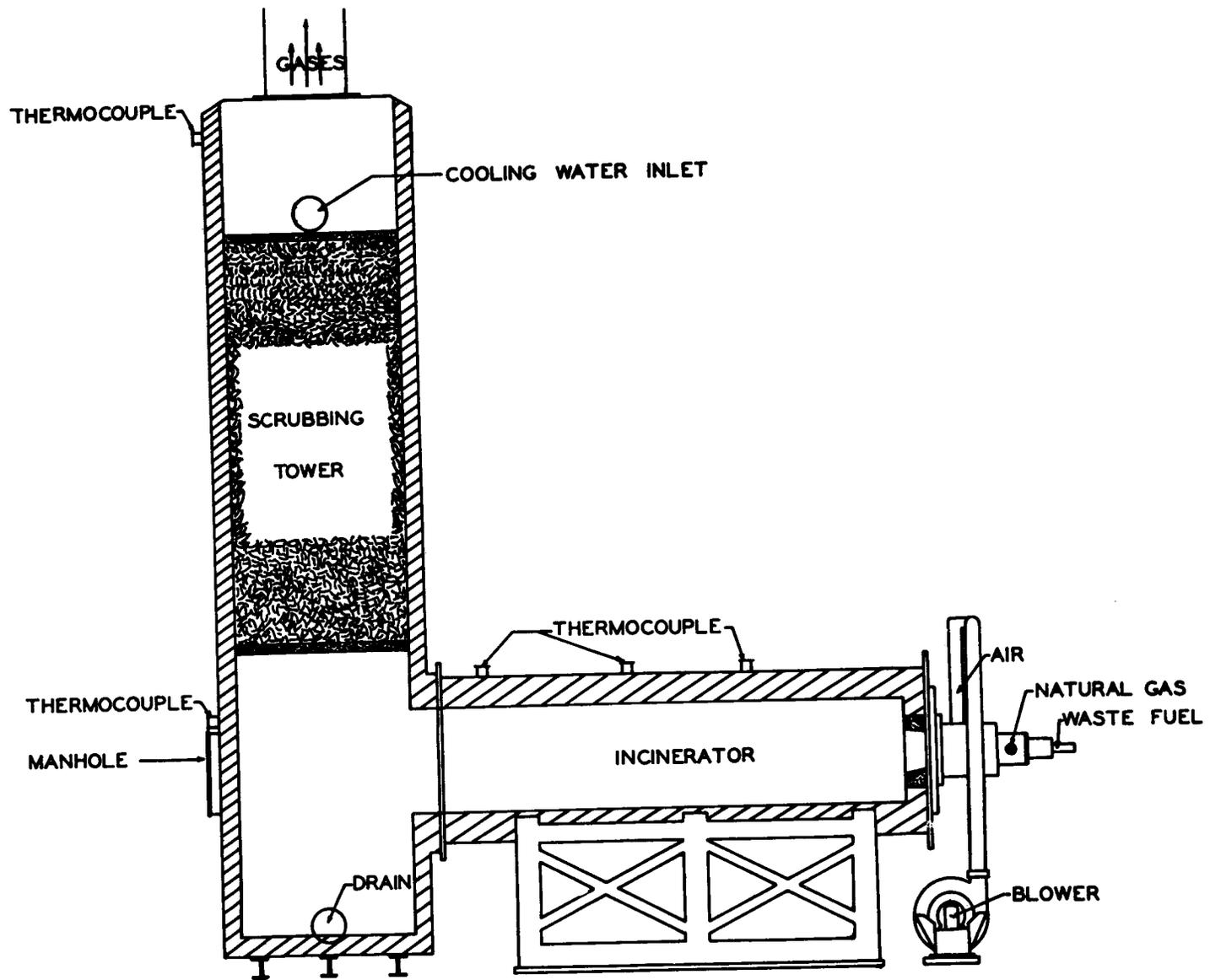


FIGURE VI: EXTERIOR VIEW OF THERMAL DESTRUCTOR COMPLEX



DRES. PHOTO

FIGURE VII: SCHEMATIC OF INTERIOR OF THERMAL DESTRUCTOR



THERMAL DESTROYER

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1. ORIGINATING ACTIVITY DEFENCE RESEARCH ESTABLISHMENT SUFFIELD		2a. DOCUMENT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP	
3. DOCUMENT TITLE DESTRUCTION AND DISPOSAL OF CANADIAN STOCKS OF WORLD WAR II MUSTARD GAS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Special Publication			
5. AUTHOR(S) (Last name, first name, middle initial) Weaver, R.S., C. Reichert and S.B. Mellisen			
6. DOCUMENT DATE December 1975		7a. TOTAL NO. OF PAGES 22	7b. NO. OF REFS 0
8a. PROJECT OR GRANT NO. 99-30-15		9a. ORIGINATOR'S DOCUMENT NUMBER(S) Suffield Special Publication No. 67	
8b. CONTRACT NO.		9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)	
10. DISTRIBUTION STATEMENT UNCLASSIFIED/UNLIMITED			
11. SUPPLEMENTARY NOTES (NON-CONTROLLED GOODS) DMC A REVIEW: GCEC December 2013		12. SPONSORING ACTIVITY	
13. ABSTRACT 50 Early in World War II, over 700 tons of the chemical warfare agent mustard were shipped from Cornwall, Ontario, to the Defence Research Establishment Suffield, [and stored in lead-lined concrete vaults.] Research was begun several years ago to find a safe, efficient, environmentally acceptable and economical method of disposing of this still hazardous material. Laboratory studies led to the discovery that, with turbulent mixing and proper control of temperature and acidity, mustard would react with water to produce a non-vesicant hydrolysate mixture. These results were extended and the process further optimized in pilot plant runs, involving a total of several tons of mustard. It was also demonstrated that the hydrolysate could be burned completely in a specifically modified incinerator.//			

KEY WORDS

1. Mustard gas
2. Hydrolysate
3. Thiodiglycol
4. Chemical warfare agent
5. Incineration
6. Thermal Destructor
7. Hydrolysis
8. Disposal

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the organization issuing the document.
- 2a. **DOCUMENT SECURITY CLASSIFICATION:** Enter the overall security classification of the document including special warning terms whenever applicable.
- 2b. **GROUP:** Enter security reclassification group number. The three groups are defined in Appendix 'M' of the DRB Security Regulations.
3. **DOCUMENT TITLE:** Enter the complete document title in all capital letters. Titles in all cases should be unclassified. If a sufficiently descriptive title cannot be selected without classification, show title classification with the usual one-capital-letter abbreviation in parentheses immediately following the title.
4. **DESCRIPTIVE NOTES:** Enter the category of document, e.g. technical report, technical note or technical letter. If appropriate, enter the type of document, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the document. Enter last name, first name, middle initial. If military, show rank. The name of the principal author is an absolute minimum requirement.
6. **DOCUMENT DATE:** Enter the date (month, year) of Establishment approval for publication of the document.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the document.
- 8a. **PROJECT OR GRANT NUMBER:** If appropriate, enter the applicable research and development project or grant number under which the document was written.
- 8b. **CONTRACT NUMBER:** If appropriate, enter the applicable number under which the document was written.
- 9a. **ORIGINATOR'S DOCUMENT NUMBER(S):** Enter the official document number by which the document will be identified and controlled by the originating activity. This number must be unique to this document.
- 9b. **OTHER DOCUMENT NUMBER(S):** If the document has been assigned any other document numbers (either by the originator or by the sponsor), also enter this number(s).
10. **DISTRIBUTION STATEMENT:** Enter any limitations on further dissemination of the document, other than those imposed by security classification, using standard statements such as:
 - (1) "Qualified requesters may obtain copies of this document from their defence documentation center."
 - (2) "Announcement and dissemination of this document is not authorized without prior approval from originating activity."
11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document, even though it may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall end with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (TS), (S), (C), (R), or (U).

The length of the abstract should be limited to 20 single-spaced standard typewritten lines; 7/8 inches long.
14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a document and could be helpful in cataloging the document. Key words should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context.